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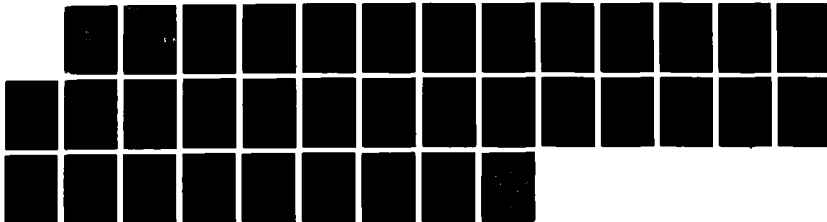
RESIST POLYMERS 9 THERMOLYSIS OF CHLORINE CONTAINING
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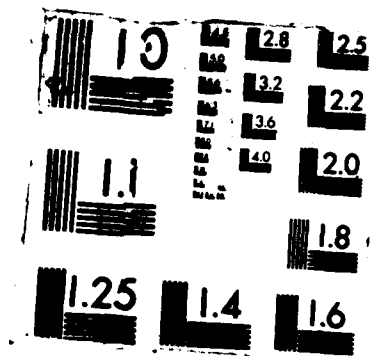
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Resist Polymers IX.

Thermolysis of Chlorine Containing Acrylate Polymers

by

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Resist Polymers IX. Thermolysis of Chlorine Containing
Acrylate Polymers

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ABSTRACT

The thermal degradation of poly(chloroethyl methacrylate) (PCEMA), poly(trichloroethyl methacrylate) (PTCEMA), poly(methyl-^{alpha}-chloroacrylate) (PMCA) and their copolymers with methyl methacrylate (MMA) have been investigated. Both ester decomposition and main chain scission occurs for the chloroalkyl methacrylate polymers with the former playing the dominant role. In contradistinction, HCl elimination and aromatization prevail over other processes for PMCA. The thermolysis results are compared with radiolysis results.

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INTRODUCTION

Photolithography has been pushed to its limits by the ever increasing demand for higher sensitivity and contrast in the manufacturing of VLSI devices. Electron beam lithography looms as one of the techniques to pack more circuitry into a smaller area. This has renewed academic as well as practical interests in the radiation chemistry of resist polymers, in particular the role of chemical structures and steric configuration in affecting susceptibility toward radiolysis. Since poly(methyl methacrylate) is the industry standard for positive E-beam resists, there have been several extensive studies on the effect of substituents in acrylate polymers on the radiation sensitivity toward chain scission and crosslinking. Fluorine and chlorine containing substituents tend to increase scission yield by radiation as has been found for polymers and copolymers of methyl- α -chloroacrylate,¹⁻³ methyl- α -fluoroacrylate,⁴ haloalkyl- α -chloroacrylate,^{5,6} and haloalkyl methacrylates.⁷

Thermal degradation of a resist is as important as its radiation sensitivity. This is because there are several thermal treatments during the manufacturing of VLSI devices, and the requirement for thermal stability is increasing for higher temperatures. This makes it necessary to make parallel studies of a polymer resist candidate for both radiolysis and thermolysis processes. The results would also benefit the understanding of the mechanisms of degradation by heat and by radiation. In our

two previous papers,^{8,9} the thermolysis of fluoro and chloro methacrylates were reported. In this paper we present the results of thermal degradation of homopolymer and copolymers of α -chloroacrylate and comparison with previously published radiolysis results.^{3,6}

EXPERIMENTAL

The synthesis of 2-chloroethyl methacrylate⁷ (CEMA) 2,2,2-trichloroethyl methacrylate³ (TCEMA) and methyl- α -chloroacrylates¹⁰ (MCA) and their polymerizations were as given previously. Thermal pyrolysis was determined by thermogravimetric analysis using a Perkin-Elmer thermobalance in N₂ atmosphere, and the pyrolysates identified by GC-MS.⁸

RESULTS AND DISCUSSION

Poly(trichloroethyl methacrylate) (PCEMA). TGA curve of

Fig. 1

PCEMA (Figure 1) shows its weight loss to begin at 250°. At 265°, 307°, 327° and 348° the wt. losses are 10, 30, 50 and 70%, respectively. The maximum decomposition rate was found to be 314° and decomposition is complete at 445°. These thermal behaviors are reproducible except the onset decomposition temperature is different for independently prepared samples of the same polymer possibly due to residual monomer and solvent.

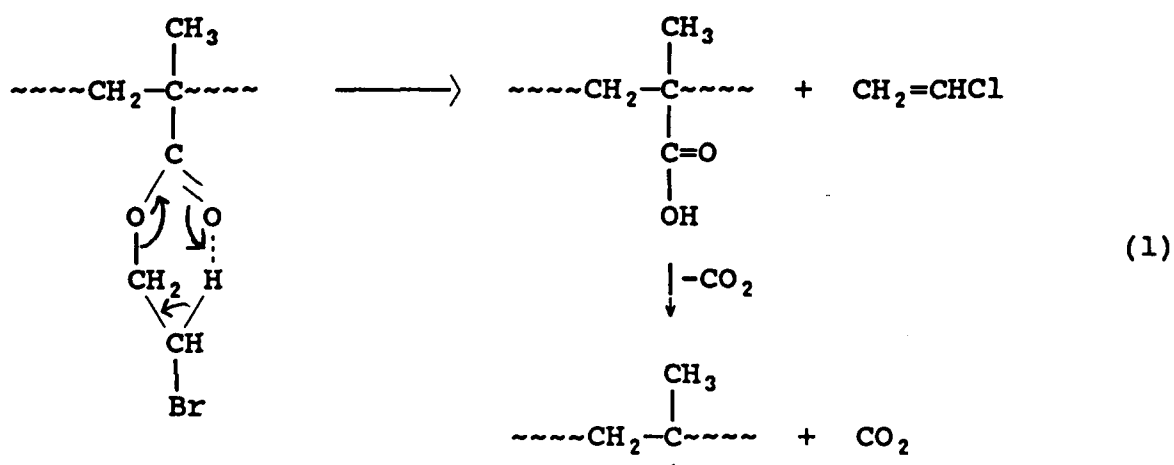
Fig. 2

Figure 2 is the pyrogram of PCEMA; the pyrolysis products

Table I

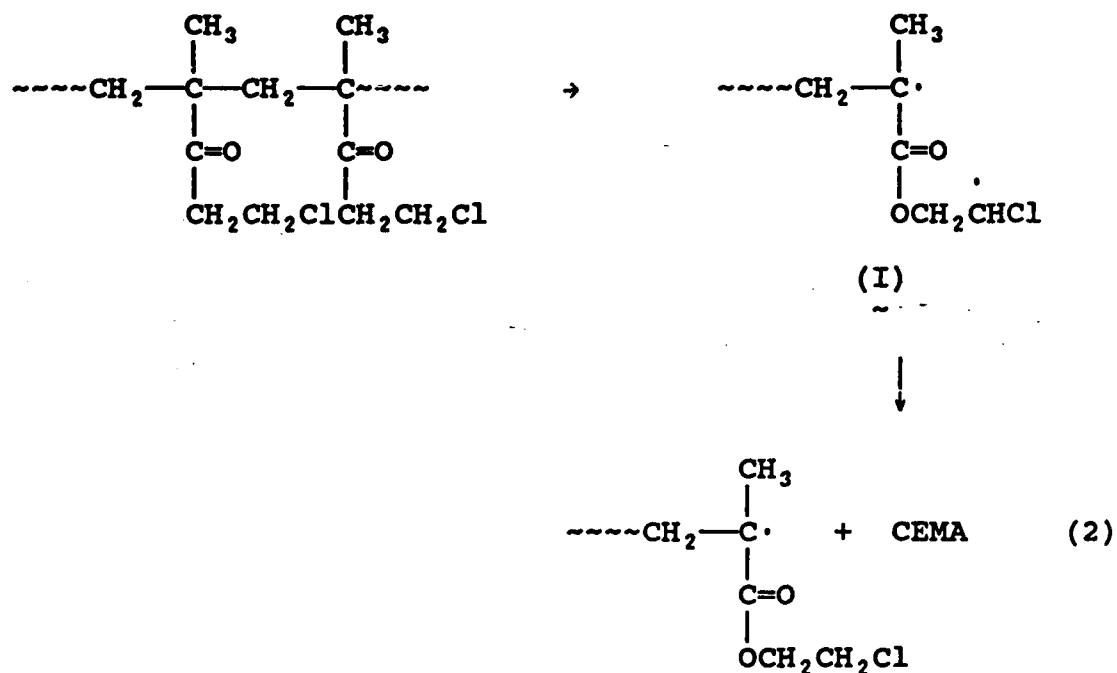
identified by MS are summarized in Table I. The most abundant

non-chlorinated products are CO_2 and acetaldehyde. Among the chlorinated products are vinyl chloride, ethyl chloride and monomer (CEMA). The formation of vinyl chloride may be attributed to the decomposition of ester groups through a six membered ring intermediate involving β -hydrogen atoms,¹¹



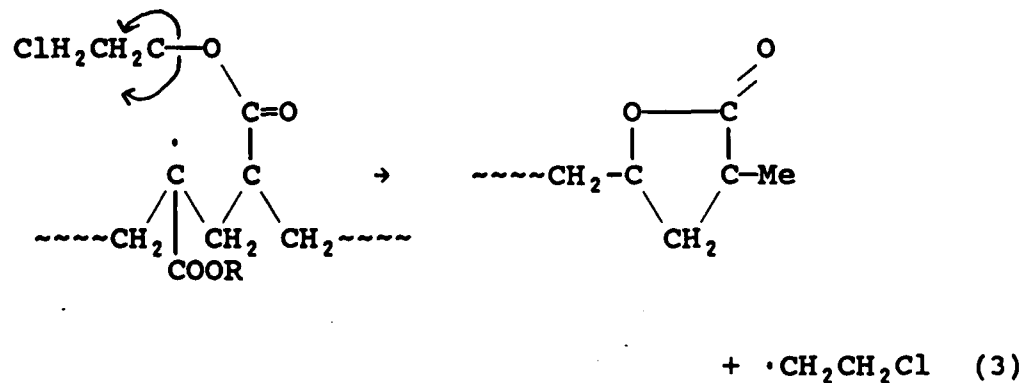
This process also produces CO_2 . The concerted mechanism shown above might be promoted by the acidic β -hydrogen and is consistent with the thermolysis results of halopenated methacrylate polymers i.e. poly(2-bromoethyl methacrylate)⁹ and poly(2-fluoroethyl methacrylate).⁸

The production of monomer is accounted for on the basis of random scission of main chains followed by depolymerization.

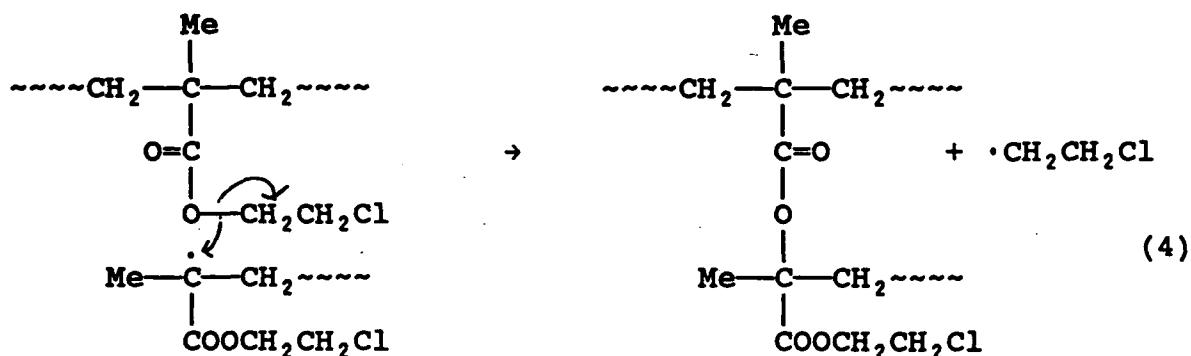


The propagating radical $\underline{\text{I}}$ may undergo intra and intermolecular reactions resulting in the liberation of ethyl chloride as shown in equations 3 and 4,

intramolecular

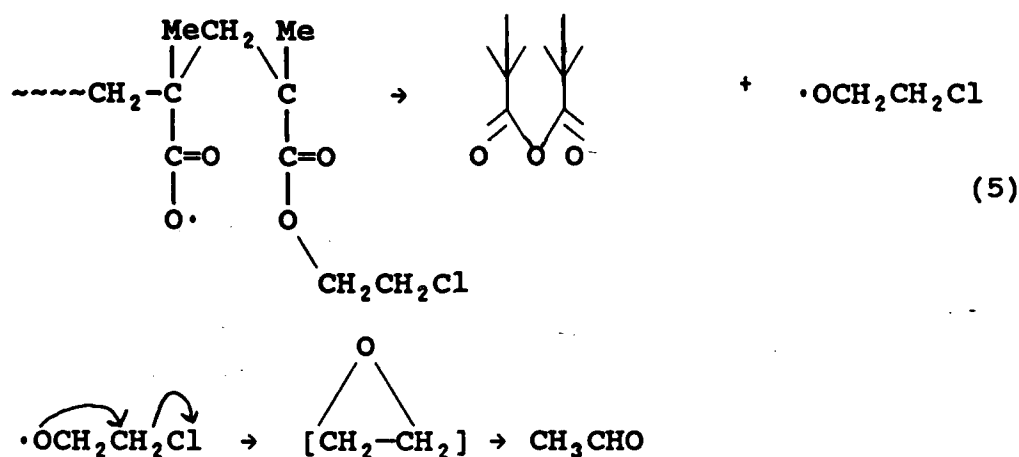


intermolecular



Formation of chloroethyl radicals is favoured over chloromethyl radicals because of the stability of the former.¹²

Production of low concentration of acetaldehyde may result from either one of the following degradation mechanisms. Intra and intermolecular reactions shown in equations 3 and 4 may produce acetaldehyde. However, in order for the acetaldehyde to be formed from γ -lactone it involves the scission of three carbon-carbon bonds and acquisition of two hydrogen atoms which is deemed improbable. A more plausible source of acetaldehyde may be the chloroethyl radical produced by the intramolecular perception in equation 5



This reaction sequence has been proposed for the pyrolysis of poly(2-fluoroethyl methacrylate).⁸

Methyl Methacrylate-chloroethyl Methacrylate Copolymers. The

pyrogram of poly(72 MMA-co-28 CEMA) is shown in Figure 3. The pyrolysis products of the copolymer are CO₂, acetaldehyde, vinyl chloride and methyl methacrylate (Table II). The abundance of MMA monomer liberated is not unexpected considering that the copolymer contains large blocks of MMA interspersed with CEMA units. On the other hand, it is difficult to explain at this juncture why the CEMA monomer was not seen in the copolymer degradation which was found in the pyrolysis of PCEMA. The other pyrolysis products are the same for the homopolymer and copolymer.

The radiolysis of poly(13 MMA-co-87 CEMA) differs from the thermolysis of poly(78 MMA-co-22 CEMA) mainly in the production

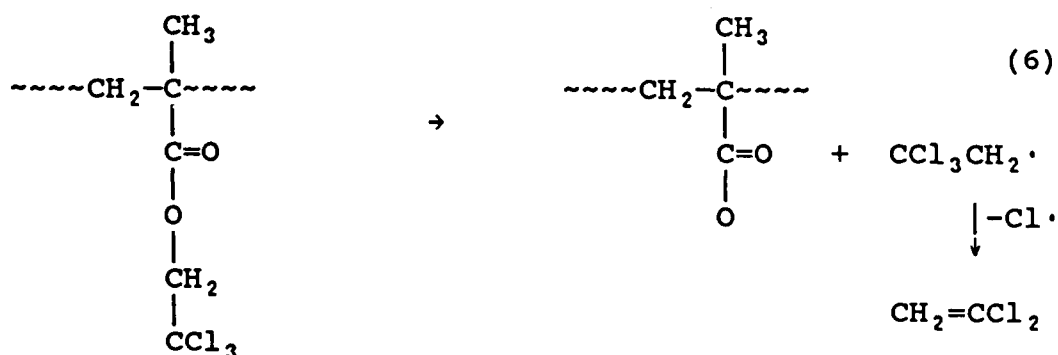
of HCl and CH_3Cl by high energy radiation. Dissociative electron capture followed by hydrogen abstraction is undoubtedly the process leading to HCl. Similar phenomenon was observed for γ -irradiated poly(bromoethyl methacrylate), but not in the case of poly(fluoroethyl methacrylate) presumably due to the strong C-F bond. Radiolysis also produces $\text{ClCH}_2\cdot$ radical to form CH_3Cl upon hydrogen abstraction. Both radiolysis and thermolysis of poly(MMA-co-CEMA) produces CO_2 , propene and ethyl chloride which implies ester decomposition occurs in both cases, but not necessarily through the same mechanism.

Poly(2,2,2-trichloroethyl methacrylate) (PTCEMA). TGA of PTCEMA showed two stages of weight loss (Fig. 4). The onset of decomposition was at 195° followed by rapid decomposition until 225° , but slowed down between 225° and 275° . The remaining material degraded rapidly above 275° . The initial stage of degradation was presumably due to dissociation of the bulky CCl_3 group which can account for 40% weight loss.

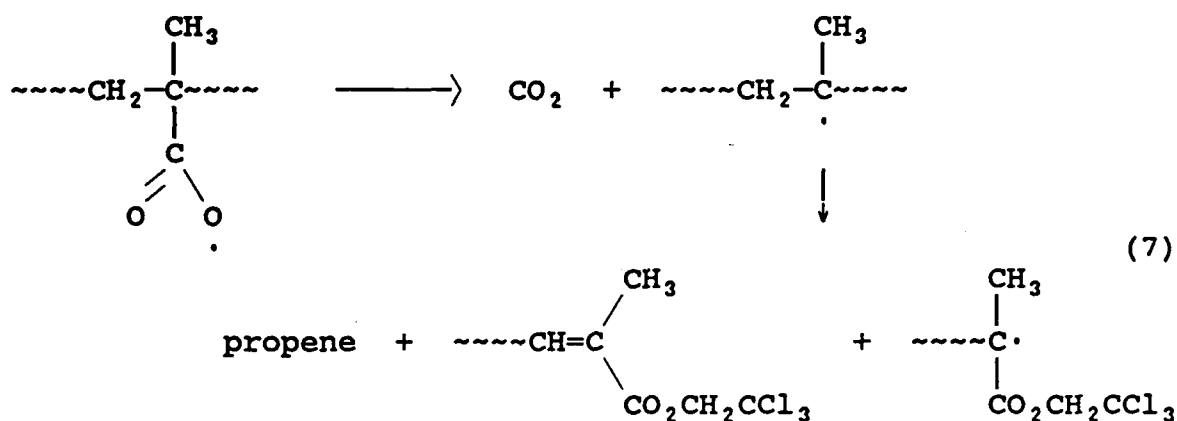
The pyrogram of PTCEMA is given in Figure 5 and the products of decomposition are summarized in Table III. The principal products are CO_2 , propene, vinyl chloride and vinylidene chloride. The absence of monomer among the pyrolysates suggests that ester decomposition is an important pathway for the degradation, probably facilitated by the polar CCl_3 groups and stability of the $\text{Cl}_3\text{C}\cdot$ radical. The molecular elimination of

vinyl chloride via a transition state proposed for PCEMA (eqn. 1) is not available to PTCMA which is devoid of β hydrogen. The actual amount of vinyl chloride found is very small (Figure 5); it is probably the result of secondary reactions.

The major pyrolysis product is vinylidene chloride. It is most likely to be produced by the elimination of the stable $\text{CCl}_3\text{CH}_2\cdot$ radical facilitated by the electron withdrawing effect of the CCl_3 group.

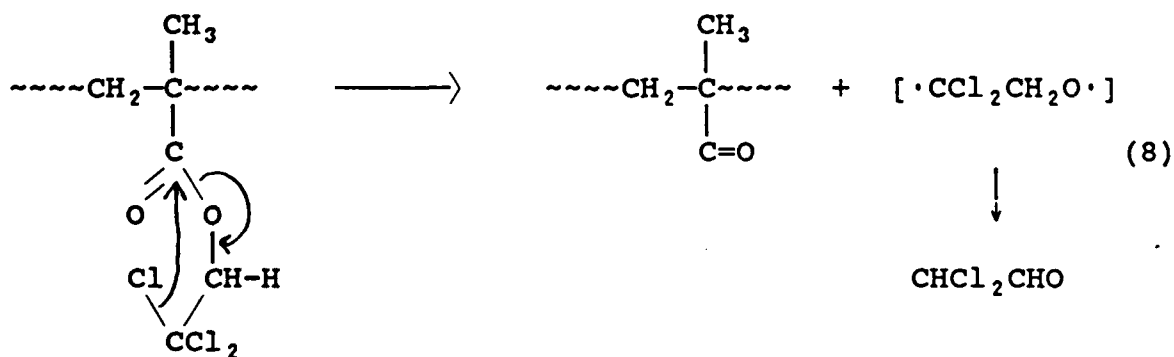


Decarboxylation and subsequent processes can produce the other products

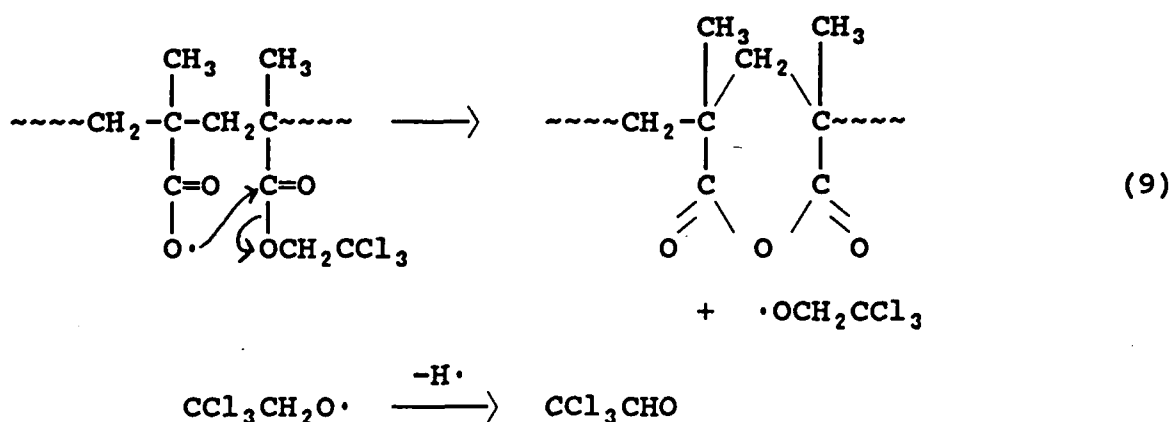


A similar decomposition mechanism had been proposed for poly(trifluoroethyl methacrylate).⁸

Though dichloroacetaldehyde was not found among the pyrolysates of PTCEMA, it was separated and identified in the thermal decomposition of TCEMA/MMA copolymer (*vide infra*). This signals the following reaction course,



It seems that chloral should be formed but not detected in the thermolysis of PTCEMA by a plausible mechanism



We can only speculate that chloral may undergo C-Cl bond cleavage and the $\cdot\text{CCl}_2\text{CHO}$ radical abstracts a hydrogen atom to provide a second possible source for the formation of dichloroacetaldehyde.

Irradiation of PTCEMA⁷ gave CO, CO₂, HCl, CH₃Cl, chloroform and various other minor products. CO₂ was the only product common to radiolysis and thermolysis. Whereas ester decomposition predominates in the latter, dissociative electron capture producing Cl \cdot and Cl₃C \cdot radicals seems to dominate in the former. Radiolysis apparently does not produce significant amounts of CCl₃CH₂ \cdot radical which would have lead to vinylidene chloride according to eq. 6 but it was not found.

The pyrogram of poly(76 MMA-co-24 TCMA) is illustrated in Figure 6; the pyrolysis products listed in Table IV. They are as one would expect, i.e. MMA plus the pyrolysates of TCMA unit. In addition there was dichloroacetaldehyde formed as discussed above. The fact that it is not observed in the decomposition of the homopolymer may be attributed to the steric hindrance of the

Fig. 6
Table IV

CCl_3 group inhibiting the formation of cyclic transition states postulated in eqs. 9 and 10.

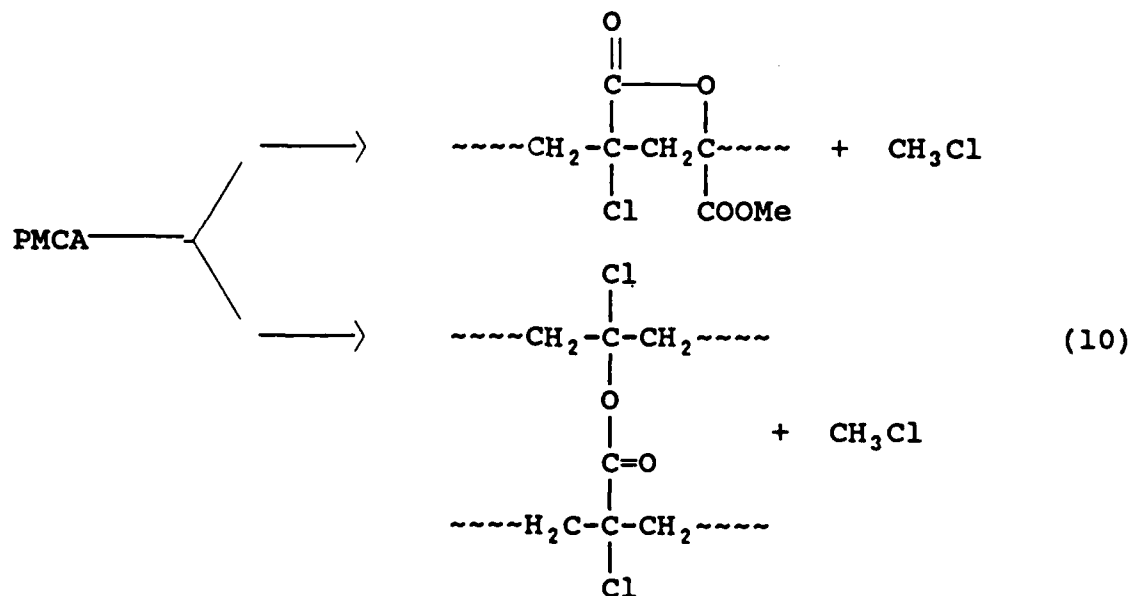
Fig. 7 Poly(methyl- α -chloroacrylate). The TGA curve (Figure 7) showed PMCA to be appreciably more stable than PCEMA or PTCEMA. Even though weight loss commences at 225° and degradation was relatively rapid initially, it slows down considerably 32% decomposition. At 265° , 295° , 360° and 420° the weight losses are 10, 30, 50 and 70%. About 20% of the polymer remained even at 475° . Since PMCA contains 34% of H + Cl, it appears that the initial thermolysis is the elimination of HCl. The residues not decomposed at 475° are carbonaceous char. If dehydrochlorinations convert the backbone carbon atoms to charry products, they would amount to 20% in agreement with the TGA data. Therefore the thermolysis processes for PMCA are distinctly different from the other two polymers with Cl in the pendant groups.

In order to find supporting evidences, PMCA was heated to 175° and IR spectra was obtained. A weak olefinic band at 1625 cm^{-1} was found as expected. The formation of the first olefinic group is known¹³ to promote the further elimination of adjacent HCl as in the thermal decomposition of poly(vinyl chloride). One might anticipate similar processes of HBr elimination would be even easier for poly(methyl- α -bromoacrylate).¹⁴ That this was found not to be the case⁹ may be due to the fact that dehydrochlorination is a chain reaction but dehydrobromination is

not. Apparently, the bromine atom is less reactive and prefers the reaction forming CH_3Br .

Fig. 8
Table V

The pyrogram (Figure 8 and Table V) showed that CH_3Cl instead of HCl was one of the major products. This may be rationalized by the acidolysis of PMCA. An alternative explanation is that HCl reacts in the column and was not eluted and that CH_3Cl was instead formed by lactonization or crosslinking,



The fact that a lactone group was not found in the IR of degraded PMCA tends to favor the first explanation rather than the latter.

Production of monomer might have resulted from random scission of main chains. This is conceivable considering the high polarization of C-C main chain bond by the chlorine atom attached to one of the carbons. It is recalled that thermolysis

of PMBA did not yield any monomer.

Fig. 9 The pyrogram of poly(62 MMA-co-38 MCA) (Figure 9) showed that it differs from that homopolymer of MCA (Figure 8) only in that MMA is produced instead of MCA (Table VI). However, because of the similarity in retention times of the two monomers, it is not easy to separate small amounts of MCA from MMA.

The products of radiolysis and pyrolysis data of PMCA suggests that a similar degradation mechanism is operative in both the processes. The principal difference is in the monomer formation. The chain terminal radical, which is believed to be involved in the unzipping process leading to monomer at the higher temperatures of thermal degradation, not not observed at ambient temperature in radiolysis. Any monomer produced can not diffuse away in the solid polymer and it may repolymerize because of the propagation-depropagation equilibrium



Acknowledgement

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Figure Captions

Figure 1 TGA of PCEMA.

Figure 2 Pyrogram of PCEMA.

Figure 3 Pyrogram of poly(78 MMA-co-22 CEMA).

Figure 4 TGA of PTCEMA.

Figure 5 Pyrogram of PTCEMA.

Figure 6 Pyrogram of poly(76 MMA-co-24 TCEMA).

Figure 7 TGA of PMCA.

Figure 8 Pyrogram of PMCA.

Figure 9 Pyrogram of poly(62 MMA-co-38 MCA).

Table I. Pyrolysates of PCMA

Peak	Compounds
1	CO ₂
2	Propene
3	Vinyl Chloride + Acetaldehyde
4	Ethyl chloride
5	Unidentified
6	CEMA

Table II. Pyrolysates of Poly(78 MMA-co-22 CEMA)

Peak	Compounds
1	CO ₂
2	Propene
3	Vinyl chloride + Acetaldehyde
4	Ethyl chloride
5	MMA

Table III. Pyrolysates of PTCMA

Peak	Compounds
1	CO ₂
2	Propene
3	Vinyl chloride
4	Vinylidene chloride
5	Unidentified

Table IV. Pyrolysates of Poly(76 MMA-co-24 TCEMA)

Peak	Compounds
1	CO ₂
2	Propene
3	Vinyl chloride
4	Vinylidene chloride
5	Dichloroacetaldehyde
6	MMA

Table V. Pyrolysates of PMCA

Peak	Compounds
1	CO ₂
2	Propene
3	CH ₃ Cl
4	Monomer (MCA)

Table VI. Pyrolysates of Poly(62 MMA-co-38 MCA)

Peak	Compounds
1	CO ₂
2	Propene
3	CH ₃ Cl
4	MMA

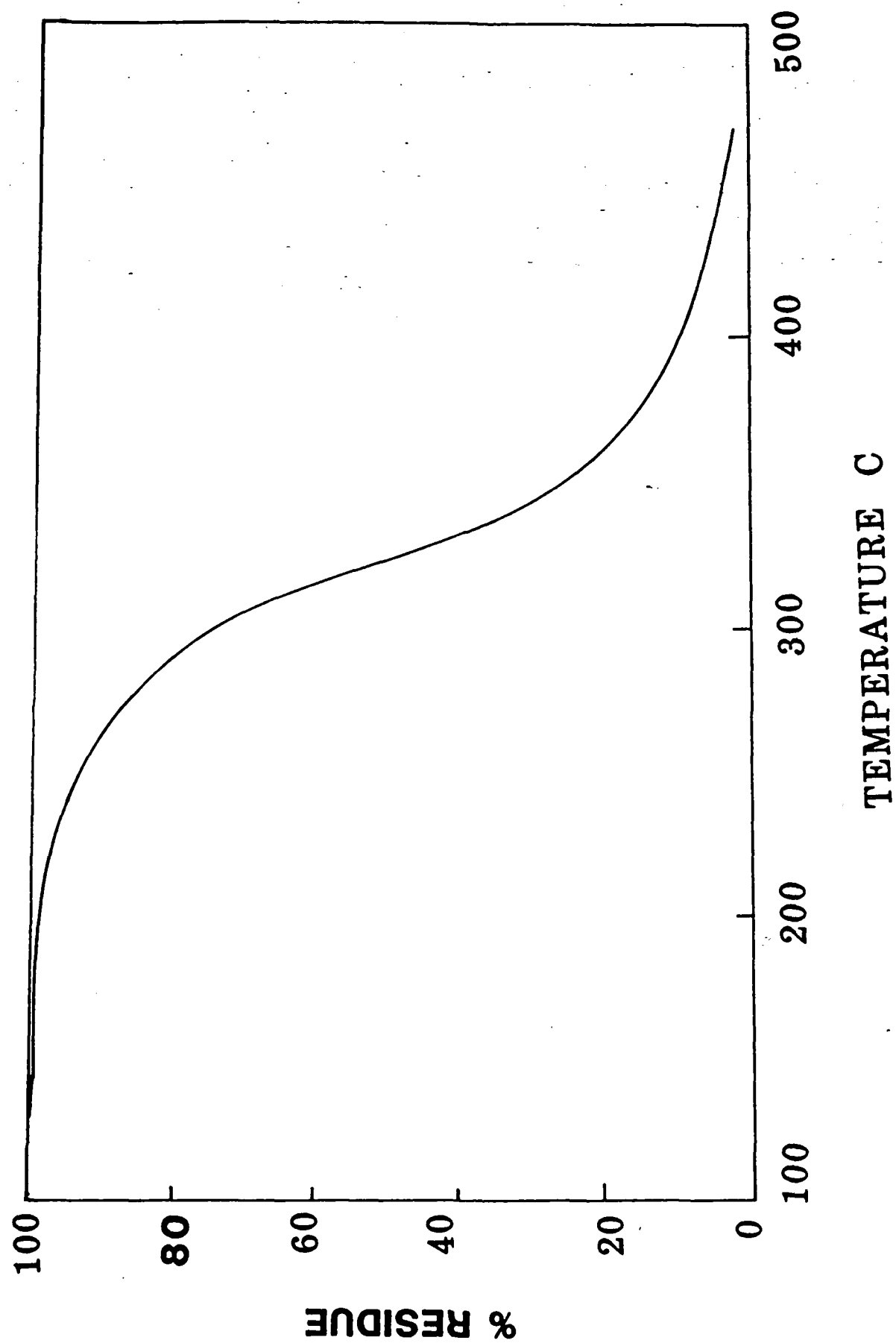


FIG.1

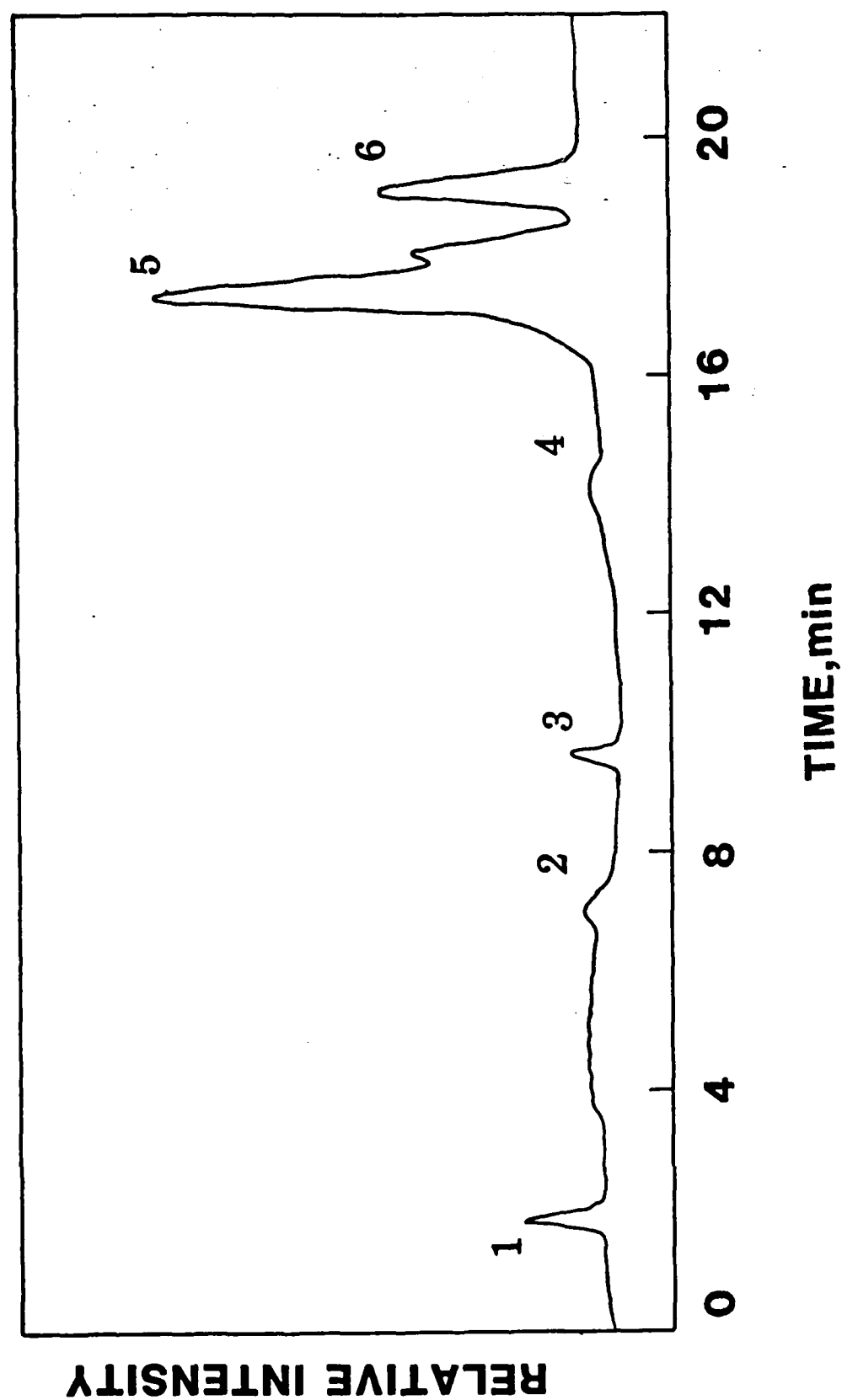


FIG.2

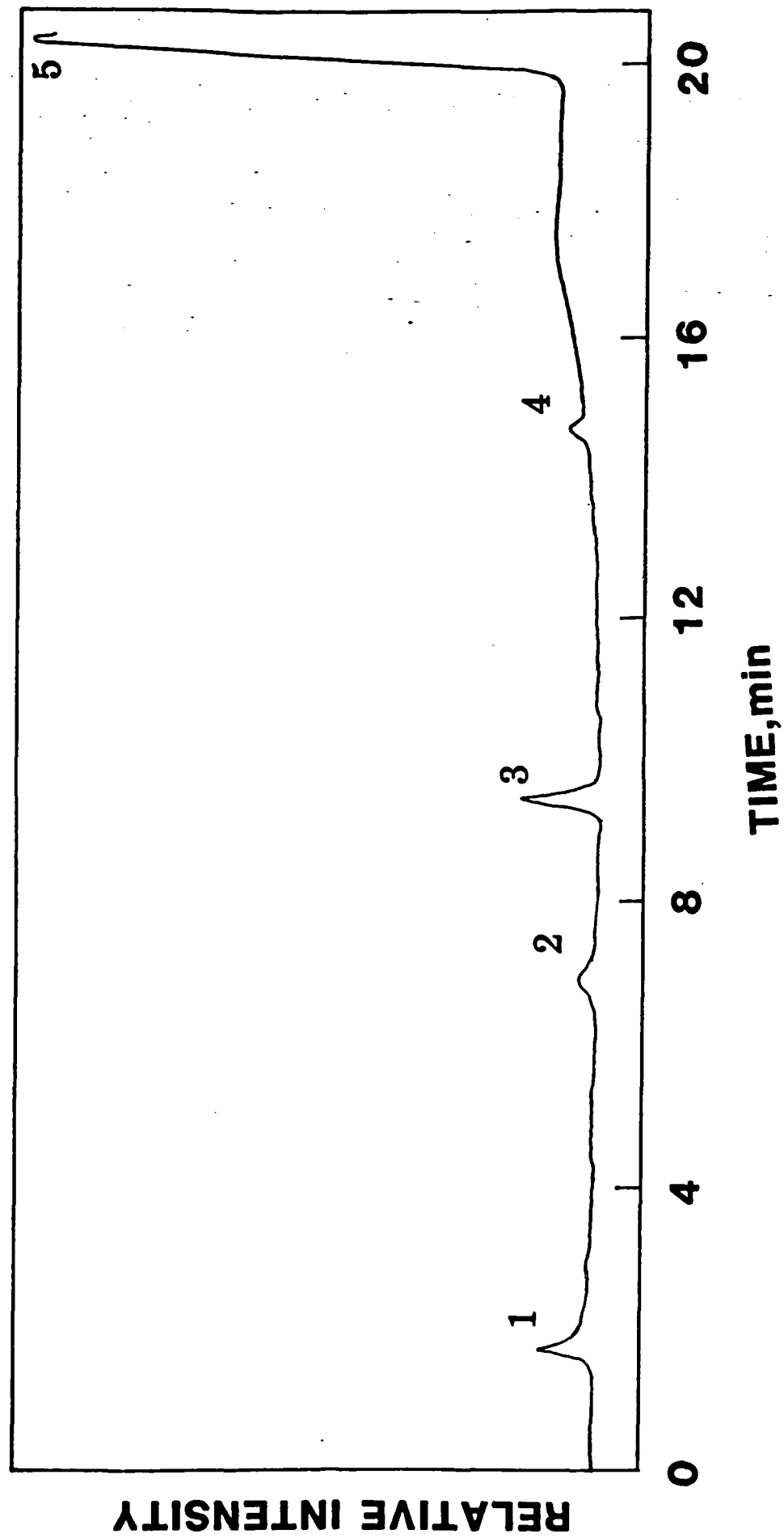


FIG.3

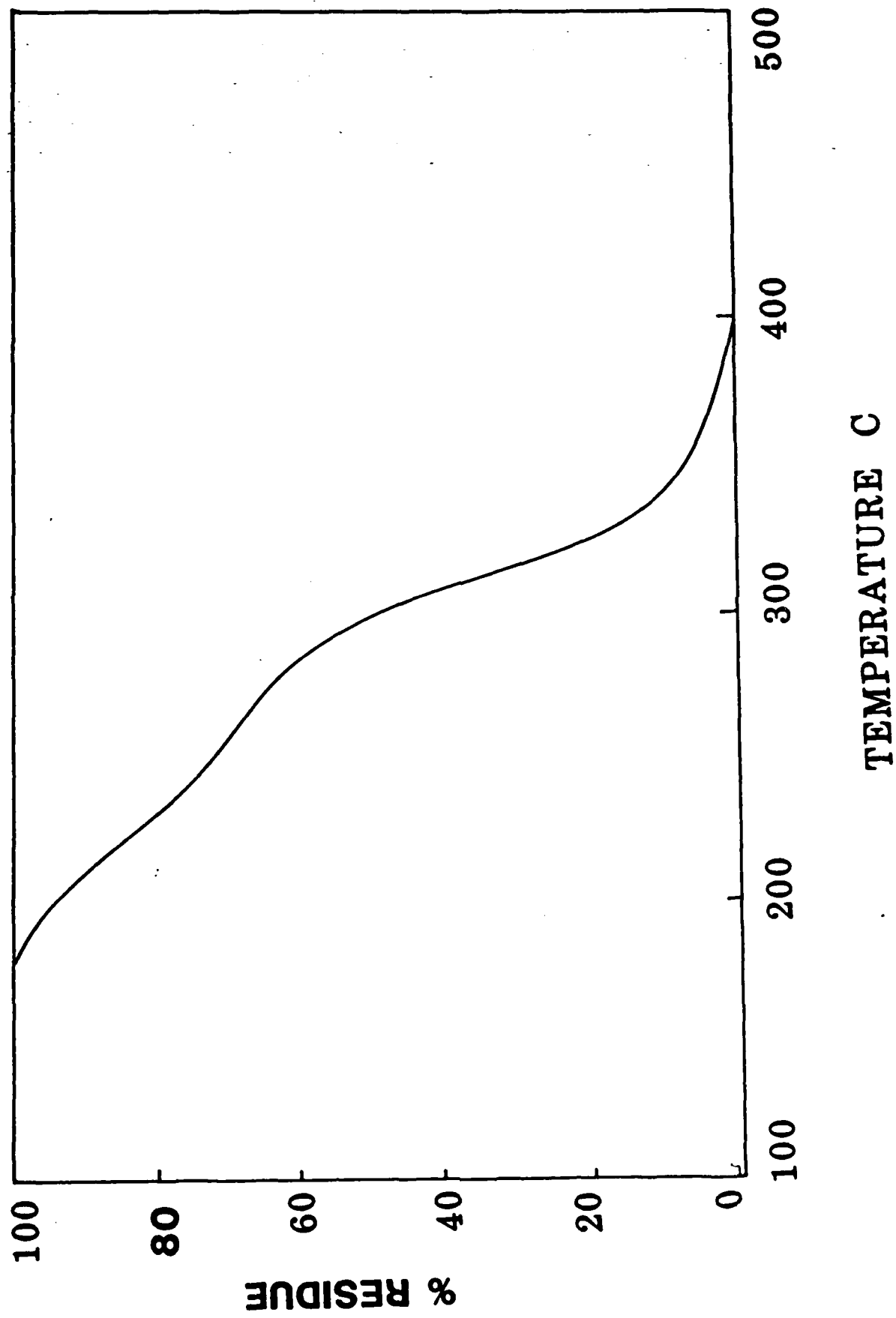


FIG.4

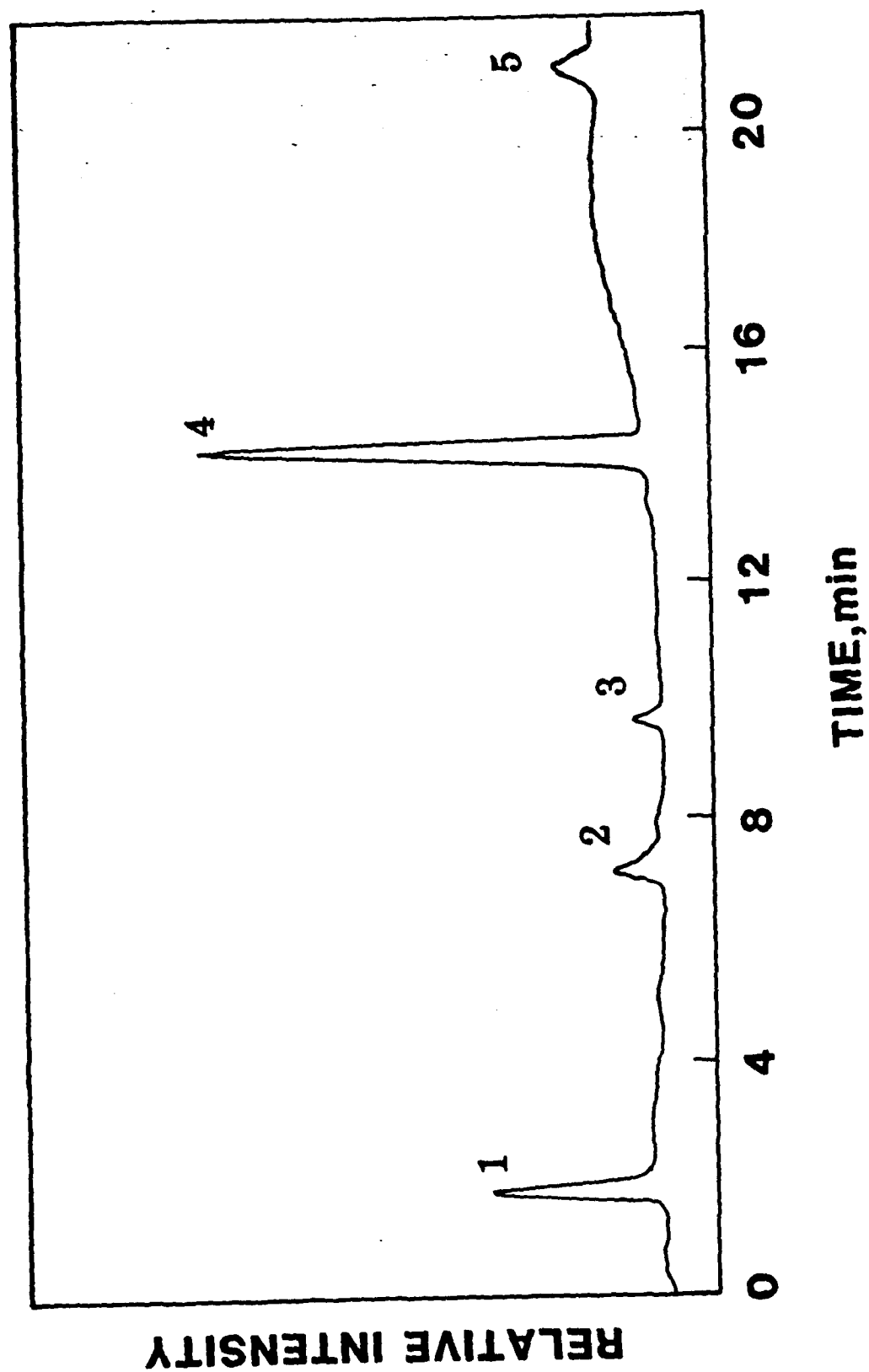


FIG.5

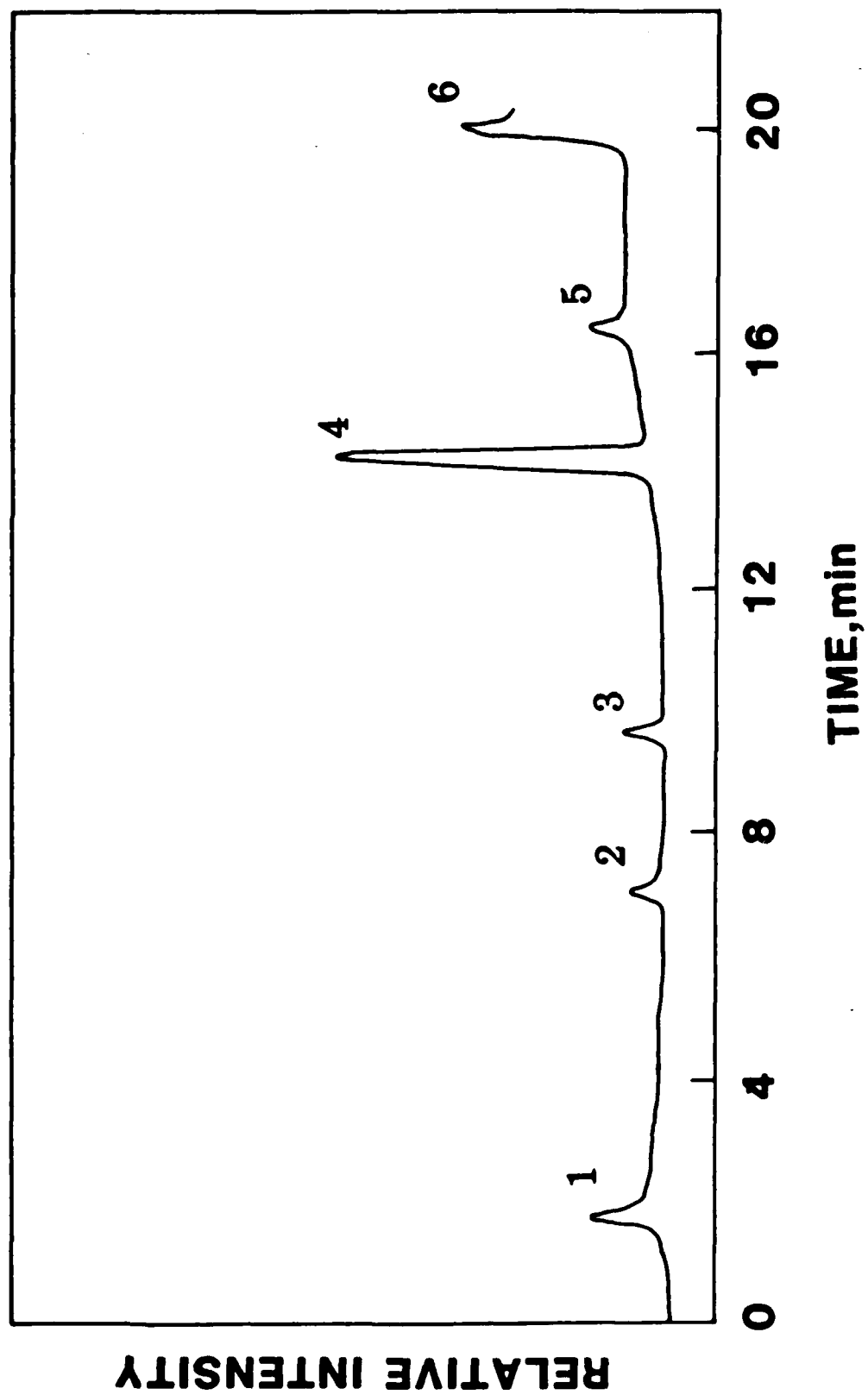


FIG.6

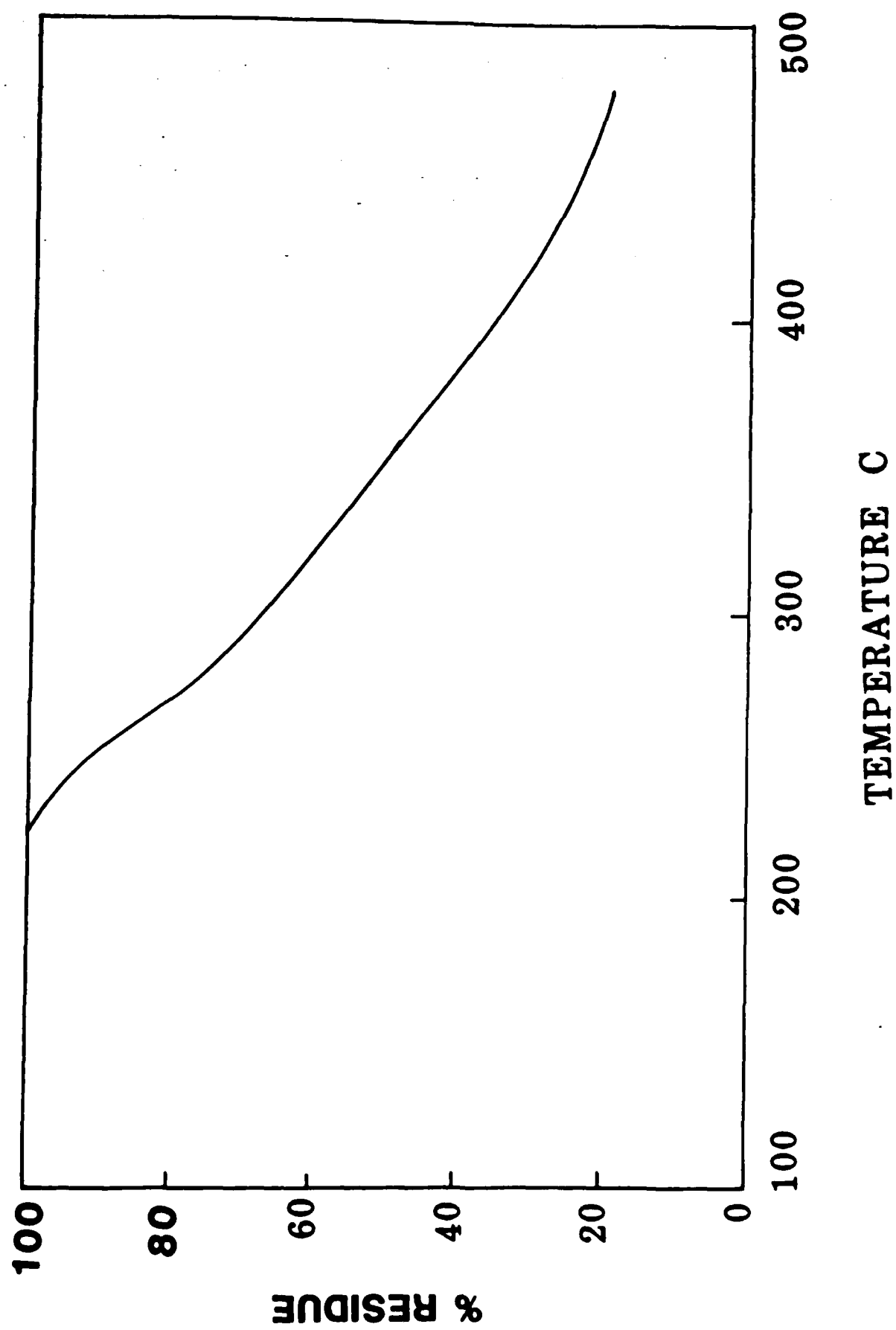


FIG.7

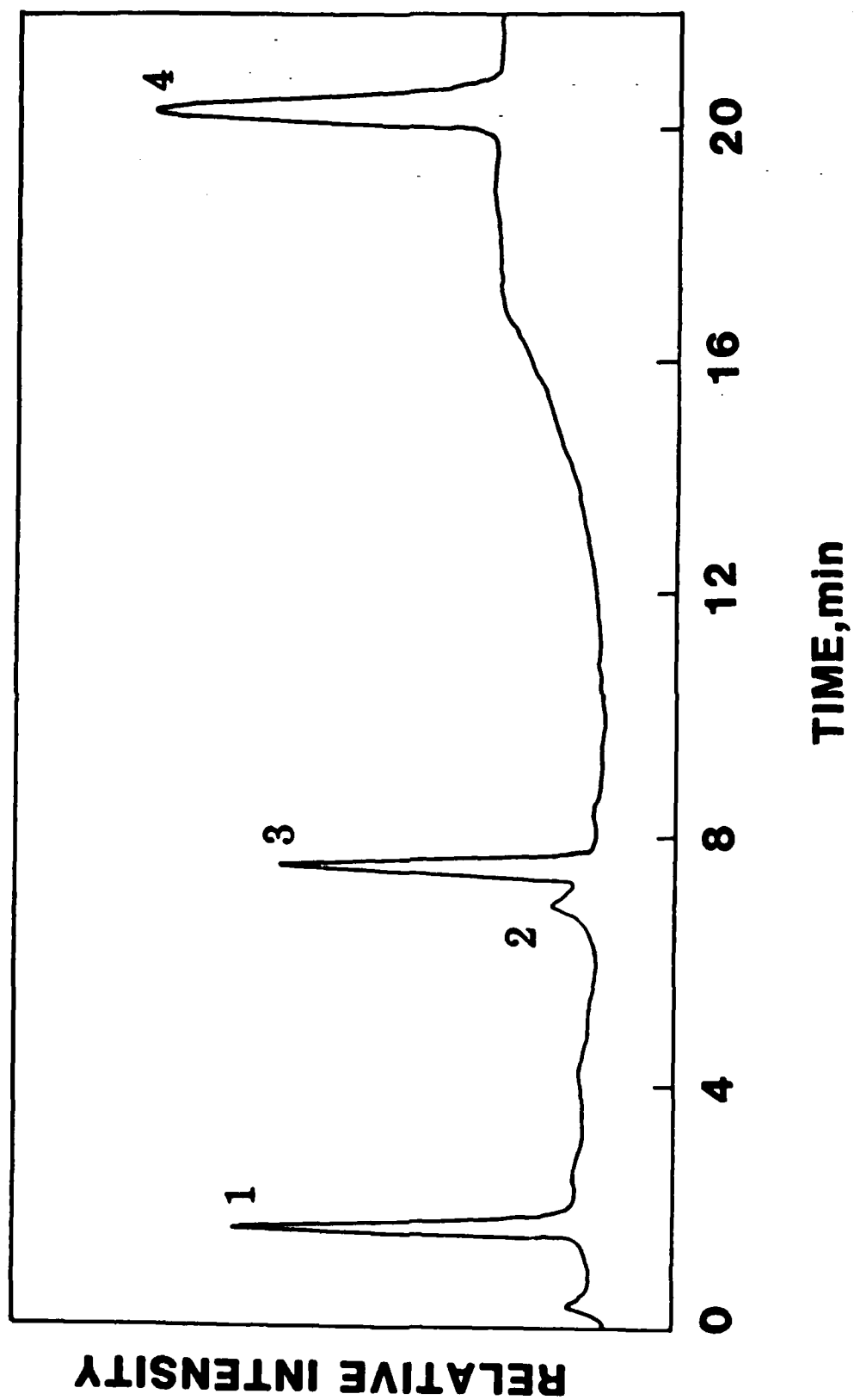


FIG.8

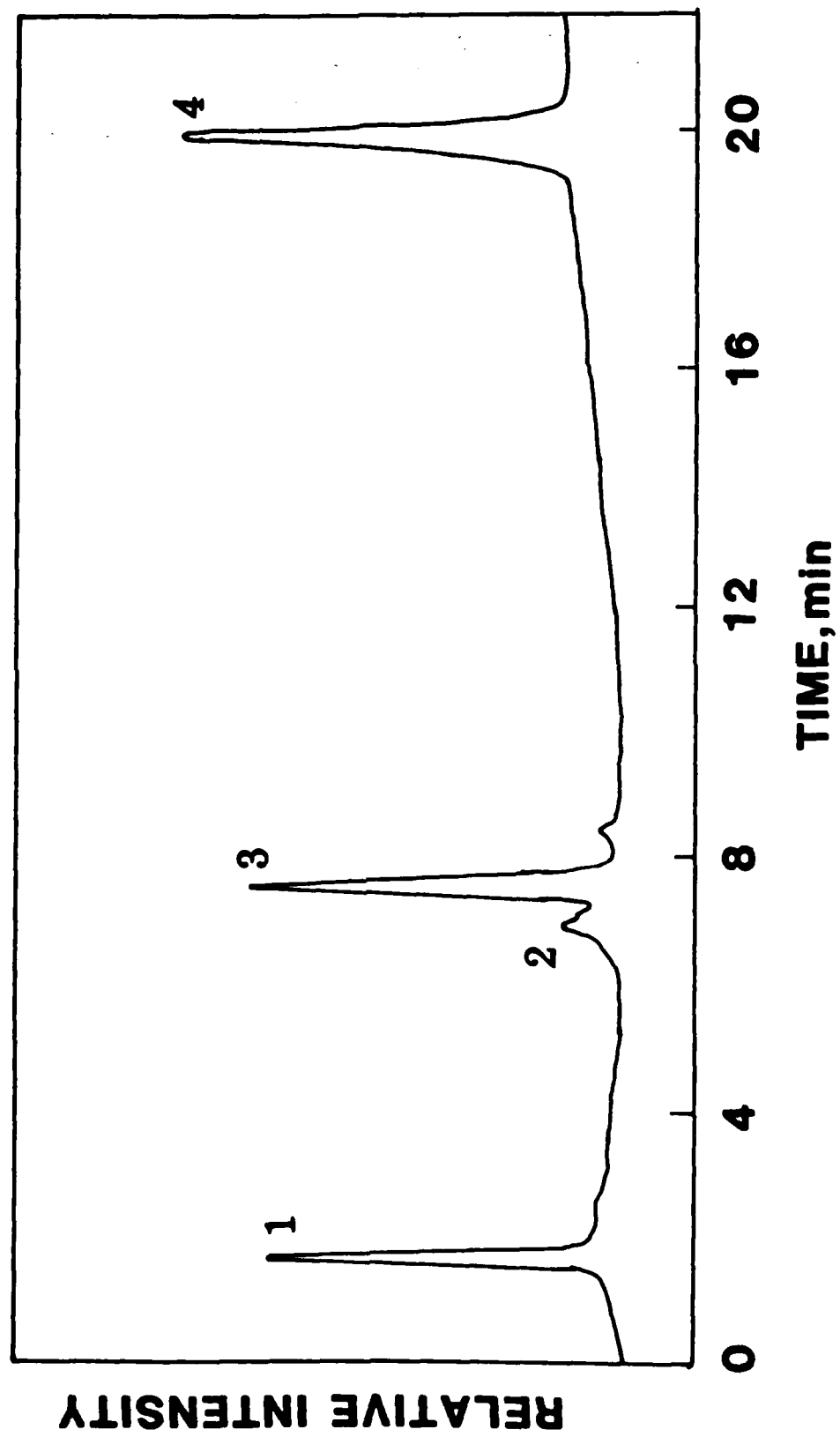


FIG. 9

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